Translation from Japanese into English

Bibliographic Data

(19)	[Publishing country]	Japan Patent Office (JP)
(12)	[Publication type]	Patent application publication (A)
(11)	[Publication number]	JP-A-Hei 11-233405
(43)	[Date of publication of application]	August 27, 1999 (Heisei 11)
(54)	[Title of the Invention]	MANUFACTURE OF SEMICONDUCTOR DEVICE
(51)	[Int. Cl.^{6}]	
		H01L 21/027 G03F 7/42 H01L 21/3065 21/306
	[FI]	
		H01L 21/30 572 B G03F 7/42 H01L 21/302 H 21/306 D S
	[Examination request]	Not requested
	[Number of claims]	5
	[Application mode]	OL
	[Number of pages]	6
(21)	[Application number]	Japanese Patent Application Hei 10-28482
(22)	[Date of filing]	February 10, 1998 (Heisei 10)
(71)	[Applicant]	
	[Identification number]	000004466
	[Name]	MITSUBISHI GASU KAGAKU KABUSHIKI GAISHA
	[Address]	TOKYO-TO CHIYODA-KU MARUNOUCHI 2 CHOME 5 BAN 2 GO
(72)	[Inventor]	
	[Name]	MARUYAMA, TAKEHITO
	[Address]	NIIGATA-KEN NIIGATA-SHI TAYUUHAMA SHINWARI 182 MITSUBISHI GASU KAGAKU KABUSHIKI GAISHA NIIGATA KENKYUUJO NAI
(72)	[Inventor]	
	[Name]	ABE, HISAOKI
	[Address]	NIIGATA-KEN NIIGATA-SHI TAYUUHAMA SHINWARI 182 MITSUBISHI GASU KAGAKU KABUSHIKI GAISHA NIIGATA KENKYUUJO NAI
(72)	[Inventor]	
	[Name]	AOYAMA, TETSUO
	[Address]	NIIGATA-KEN NIIGATA-SHI TAYUUHAMA SHINWARI 182 MITSUBISHI GASU KAGAKU KABUSHIKI GAISHA NIIGATA KENKYUUJO NAI
(57)	[Abstract]	
	[Problem to be Solved]	To provide a method of manufacturing a semiconductor device in which a remaining resist and a resist residual that remain on an inorganic substrate after dry etching in a wiring process can be removed at a low temperature in a short period without permitting the materials of wiring, an insulating film, etc., to corrode.
	[Solution]	A photoresist that remains on an inorganic substrate after dry etching is stripped by cleaning with a cleaning solution containing an oxidizing agent and an organic acid and then stripping using a resist stripper.

[Claims]

[Claim 1]

A method of manufacturing a semiconductor device, comprising the following steps performed sequentially:
(1) forming a predetermined pattern with a resist on a conductive thin film provided on a substrate;
(2) removing by dry etching an unwanted portion of the conductive thin film using the resist pattern as a mask;
(3) cleaning the substrate with a cleaning solution containing an oxidizing agent and an organic acid; and
(4) removing a remaining resist and a sidewall protection film with a resist stripper.

[Claim 2]

A method of manufacturing a semiconductor device, comprising the following steps performed sequentially:
(1) forming a predetermined pattern with a resist on a conductive thin film provided on a substrate;
(2′) removing by dry etching an unwanted portion of the conductive thin film using the resist pattern as a mask and then removing by ashing a modified resist layer which has been generated by the dry etching;
(3) cleaning the substrate with a cleaning solution containing an oxidizing agent and an organic acid; and
(4) removing a remaining resist and a sidewall protection film with a resist stripper.

[Claim 3]

The method of manufacturing a semiconductor device according to claim 1 or 2, wherein the oxidizing agent is an inorganic peroxide.

[Claim 4]

The method of manufacturing a semiconductor device according to claim 1 or 2, wherein the oxidizing agent is hydrogen peroxide.

[Claim 5]

The method of manufacturing a semiconductor device according to claim 1 or 2, wherein the organic acid is an aliphatic monocarboxylic acid or an aliphatic polycarboxylic acid.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a method of manufacturing a semiconductor device, and more specifically, to a method of efficiently manufacturing a semiconductor device in which a remaining resist and a sidewall protection film can be removed in a simple and easy manner after dry etching.

[0002]

[Related Art]

To manufacture a semiconductor device such as a semiconductor integrated circuit or a liquid crystal display device, in general, sputtering or a similar technique is used to form a conductive thin film on an inorganic substrate, and a predetermined pattern is formed with a resist on the conductive thin film by photolithography. Then, the entire substrate surface is irradiated with active light such as ultraviolet rays to cure the resist pattern. The thus obtained resist pattern (hereinafter referred to as "remaining resist") is used as a mask, and the unmasked area is dry-etched to form a wiring circuit. In general, a chlorine-based gas or a fluorine-based gas is used as a dry-etching gas. On the sidewalls of the pattern of the thus formed wiring circuit, a sidewall protection film is formed as a product of the reaction among the resist, the dry-etching gas and the conductive thin film. Anisotropic etching provided by the sidewall protection film has enabled advanced, selective etching allowing microfabrication. However, there has been a problem that the sidewall protection film is difficult to remove. In order to solve this problem, various types of resist stripper have been conventionally used to strip the remaining resist and the sidewall protection film after the dry etching. Examples of the resist stripper include those containing a phenol, a sulfonic acid, a halocarbon, an alkanolamine, etc. Along with the recent trend toward ultra-fine devices, however, etching conditions such as high-density plasma have become stricter, especially for dry etching. Therefore, the remaining resist and the sidewall protection film after dry etching contain large amounts of metal components used to form wiring, an insulating film, etc., and halogen-based gas used for dry etching. There has been another problem that the remaining resist and the sidewall protection film, which contain large amounts of halogen-based gas, etc., are difficult to remove using the stripper described above, even by stripping at a high temperature for a long period.

Stripping at a high temperature for a long period involves disadvantages such as corrosion of the wiring material, in particular for an aluminum-alloy wiring material.

[0003]

Thus, a method of manufacturing a semiconductor device has been desired in which a remaining resist and a sidewall protection film that remain after dry etching can be stripped at a low temperature in a short period without permitting the materials of wiring, an insulating film, etc., to corrode.

[0004]

[Problem to be Solved by the Invention]

In view of the foregoing, the present invention has an object to provide a method of manufacturing a semiconductor device in which a remaining resist and a sidewall protection film that remain after dry etching can be stripped at a low temperature in a short period without permitting the materials of wiring, an insulating film, etc., to corrode.

[0005]

[Means for Solving the Problem]

The present inventors have made an earnest study to solve the problems of the related art described above, and have found that a remaining resist and a sidewall protection film that remain on an inorganic substrate after dry etching can be stripped under mild conditions in a short period without permitting a wiring material, etc., to corrode, by cleaning with a cleaning solution containing an oxidizing agent and an organic acid and then stripping using a resist stripper. The present inventors have thus completed the present invention. That is, the present invention provides:

- a method of manufacturing a semiconductor device (hereinafter occasionally referred to as "manufacturing method 1"), including the following steps performed sequentially: (1) forming a predetermined pattern with a resist on a conductive thin film provided on a substrate; (2) removing by dry etching an unwanted portion of the conductive thin film using the resist pattern as a mask; (3) cleaning the substrate with a cleaning solution containing an oxidizing agent and an organic acid; and (4) removing a remaining resist and a sidewall protection film with a resist stripper, and

[0006]

- a method of manufacturing a semiconductor device (hereinafter occasionally referred to as "manufacturing method 2"), including the following steps performed

sequentially: (1) forming a predetermined pattern with a resist on a conductive thin film provided on a substrate; (2) removing by dry etching an unwanted portion of the conductive thin film using the resist pattern as a mask and then removing by ashing the resist layer which has been generated by the dry etching; (3) cleaning the substrate with a cleaning solution containing an oxidizing agent and an organic acid; and (4) removing a remaining resist and a sidewall protection film with a resist stripper.

[0007]

[Embodiment of the Invention]

The resist stripper for use in the present invention is not specifically limited and may be a generally known stripper that may be appropriately selected according to the remaining state of the resist and depending on the inorganic substrate used. Examples of the stripper include those containing as a main component an alkanolamine, a phenol, a sulfonic acid and a halocarbon such as those disclosed in JP-A-Hei 5-273768, JP-A-Hei 5-281753 and JP-A-Hei 6-266119, for example. As the oxidizing agent to be used in the cleaning solution for use in the present invention, there may be mentioned an inorganic peroxide such as hydrogen peroxide and ozone, a halogen or a halide such as chlorine and hypochlorous acid, and an organic peroxide such as benzoyl peroxide. Among these oxidizing agents, an inorganic peroxide is preferred, and hydrogen peroxide is particularly preferred. The concentration of the oxidizing agent in the cleaning solution may be 0.1 to 60 % by weight, preferably 0.5 to 30 % by weight.

[0008]

As the organic acid to be used in the cleaning solution, there may be mentioned: an aliphatic monocarboxylic acid such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, lauric acid, palmitic acid and stearic acid; an aliphatic polycarboxylic acid such as oxalic acid, malonic acid, succinic acid, maleic acid, glutaric acid, adipic acid and sebacic acid; an aromatic monocarboxylic acid such as benzoic acid and toluic acid; an aromatic polycarboxylic acid such as phthalic acid and trimellitic acid; an oxycarboxylic acid such as glycolic acid, malic acid, tartaric acid and citric acid; an amino acid such as glycin and alanine; and an aromatic sulfonic acid such as benzenesulfonic acid and toluenesulfonic acid. Among these organic acids, an aliphatic monocarboxylic acid and an aliphatic polycarboxylic acid are preferred. These acids may be used in combination of two or more kinds thereof. The organic acid may be used in an amount of 0.1 to 50 % by weight, preferably 0.5 to 30 % by weight, in the cleaning solution. The pH of the cleaning solution for use in the present

invention is not specifically limited. A surface-active agent or an alcohol may be added to the cleaning solution to improve the wettability. For example, a cationic, nonionic or anionic surface-active agent, methanol, or ethanol may be added. The cleaning temperature, at which the cleaning solution is used, is generally in the range of room temperature to 80°C, and may be appropriately selected according to the etching conditions and depending on the inorganic substrate used.

[0009]

Now, a description will be made of the methods of manufacturing a semiconductor device in accordance with the present invention. Manufacturing Method 1 is composed of Steps (1), (2), (3) and (4) described below.

In Step (1), a predetermined pattern is formed with a resist on a conductive thin film provided on an inorganic substrate. In Step (1), a conductive thin film is first formed on an inorganic substrate by sputtering, vacuum evaporation, etc., and a resist film is formed on the conductive thin film. The resist film is then exposed to an active beam for image formation, and developed to form a predetermined resist pattern on the thin film. The inorganic substrate may be composed of a semiconductor wiring material such as silicon, a-silicon, polysilicon, a silicon oxide film, a silicon nitride film, aluminum, an aluminum alloy, titanium, titanium-tungsten, titanium nitride, tungsten, tantalum, tantalum oxide, a tantalum alloy, chromium, chromium oxide, a chromium alloy and ITO (indium tin oxide), or a compound semiconductor such as gallium arsenide, gallium phosphide and indium phosphide, and a glass substrate for LCD, etc.

[0010]

In Step (2), the unmasked area, or an unwanted portion of the conductive thin film, is removed by dry etching in a known method using the resist pattern formed in Step (1) as a mask. Then, in Step (3), the surface of the inorganic substrate on which a pattern has been formed is cleaned using the cleaning solution described above. After that, in Step (4), a remaining resist and a sidewall protection film are removed using a known resist stripper.

[0011]

Manufacturing Method 2 is composed of Steps (1), (2'), (3) and (4). Steps (1), (3) and (4) are the same as those in Manufacturing Method 1 described above. In Step (2'), dry etching is followed by ashing to remove a modified resist layer which has been generated by the dry etching.

[0012]

In this way, the remaining resist and the sidewall protection film can be completely removed by cleaning using the cleaning solution, followed by rinsing. In the rinsing, ultrapure water is generally used as the rinse solution. However, other suitable solutions may be used as necessary, such as a water-soluble organic solvent such as an alcohol, a mixture of a water-soluble organic solvent and ultrapure water, and a solution added with a surface-active agent.

[0013]

[Example]

The present invention will now be described more specifically by way of examples and comparative examples. It should be noted, however, that the present invention is not limited by these examples. FIG. 1 shows a cross section of a semiconductor device in which an aluminum wiring element 4 is formed by dry etching using a resist film 6 as a mask. In FIG. 1, a semiconductor device substrate 1 is covered with an oxide film 2, and a sidewall protection film 5 is formed during the dry etching. Reference numeral 3 denotes a titanium nitride (TiN) as a barrier metal.

[0014]

Examples 1 to 8 and Comparative Examples 1 to 4

The semiconductor device illustrated in FIG. 1 was cleaned for a predetermined period using the cleaning solution specified in FIGs. 1 and 3, and immersed for a predetermined period in the stripper specified in FIGs. 1 and 3. The semiconductor device is rinsed with a rinse solution and then with water, dried, and observed with a scanning electron microscope (SEM). The stripping property of the resist film 6 and the sidewall protection film 5 and the corrosiveness of the aluminum wiring element 4 were evaluated according to the evaluation criteria below. The evaluation results are shown in Tables 2 and 4.

（剥離性）　◎：完全に除去された
△：一部残存物が認められた
×：大部分が残存していた
（腐食性）　◎：腐食は全く認められなかった
△：一部腐食が認められた
×：激しい腐食が認められた

(Stripping property)　A: Completely removed
B: Some remaining
C: Most remaining
(Corrosiveness)　A: Not corroded at all
B: Partly corroded
C: Significantly corroded

[0015]

[Table 1]

表－1

		洗浄液			洗浄条件		剥離剤		剥離条件		リンス
		酸化剤種類 濃度 (重量%)	有機酸種類 濃度 (重量%)	水 濃度 (重量%)	温度 (℃)	時間 (分)	アミン種 濃度 (重量%)	溶剤種 濃度 (重量%)	温度 (℃)	時間 (分)	
実施例	1	過酸化水素 5	シュウ酸 3	92	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	10	イソプロパノール
	2	過酸化水素 3	シュウ酸 3	94	50	5	モノエタノールアミン 70	ジメチルスルホキシド 30	70	10	イソプロパノール
	3	過酸化水素 5	シュウ酸 1	94	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	10	イソプロパノール
	4	過酸化水素 5	酢酸 7	88	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	10	イソプロパノール
	5	過酸化水素 5	マロン酸 5	90	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	10	イソプロパノール
	6	過酸化水素 10	シュウ酸 10	80	40	5	モノエタノールアミン 70	ジエチレングリコールモノメチルエーテル 30	70	10	イソプロパノール
	7	過酸化水素 3	シュウ酸 5	92	60	10	モノエタノールアミン 70	ジエチレングリコールモノブチルエーテル 30	70	10	イソプロパノール
	8	過酸化水素 1	シュウ酸 2	97	70	10	モノエタノールアミン 70	N－メチルピロリドン 70	70	10	イソプロパノール

		Cleaning solution			Cleaning conditions		Stripper		Stripping conditions		Rinse
		Oxidizing agent Concentration (% by weight)	Organic acid Concentration (% by weight)	Water Concentration (% by weight)	Temperature (°C)	Time (min)	Amine Concentration (% by weight)	Solvent Concentration (% by weight)	Temperature (°C)	Time (min)	
Example	1	Hydrogen peroxide 5	Oxalic acid 3	92	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	10	Isopropanol
	2	Hydrogen peroxide 3	Oxalic acid 3	94	50	5	Monoethanolamine 70	Dimethyl sulfoxide 30	70	10	Isopropanol
	3	Hydrogen peroxide 5	Oxalic acid 1	94	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	10	Isopropanol
	4	Hydrogen peroxide 5	Acetic acid 7	88	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	10	Isopropanol
	5	Hydrogen peroxide 5	Malonic acid 5	90	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	10	Isopropanol
	6	Hydrogen peroxide 10	Oxalic acid 10	80	40	5	Monoethanolamine 70	Diethylene glycol monomethyl ether 30	70	10	Isopropanol
	7	Hydrogen peroxide 3	Oxalic acid 5	92	50	10	Monoethanolamine 70	Diethylene glycol monobutyl ether 30	70	10	Isopropanol
	8	Hydrogen peroxide 1	Oxalic acid 2	97	70	10	Monoethanolamine 70	N-methylpyrrolidone 70	70	10	Isopropanol

[0016]

[Table 2]

表－２

		剥離性		アルミニウム４腐食性
		レジスト膜６	側壁保護膜５	
実施例	1	◎	◎	◎
	2	◎	◎	◎
	3	◎	◎	◎
	4	◎	◎	◎
	5	◎	◎	◎
	6	◎	◎	◎
	7	◎	◎	◎
	8	◎	◎	◎

		Stripping property		Corrosiveness
		Resist film 6	Sidewall protection film 5	Aluminum wiring element 4
Example	1	A	A	A
	2	A	A	A
	3	A	A	A
	4	A	A	A
	5	A	A	A
	6	A	A	A
	7	A	A	A
	8	A	A	A

[0017]

[Table 3]

表－3

		洗浄液			洗浄条件		剥離剤		剥離条件		リンス
		酸化剤種類 濃度 (重量%)	有機酸種類 濃度 (重量%)	水 濃度 (重量%)	温度 (℃)	時間 (分)	アミン種 濃度 (重量%)	溶剤種 濃度 (重量%)	温度 (℃)	時間 (分)	
比較例	1	—	—	—	—	—	モノエタノールアミン 70	ジメチルスルホキシド 30	70	20	イソプロパノール
	2	—	—	—	—	—	モノエタノールアミン 70	ジメチルスルホキシド 30	90	20	イソプロパノール
	3	過酸化水素 5	—	95	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	20	イソプロパノール
	4	-	シュウ酸 5	95	50	10	モノエタノールアミン 70	ジメチルスルホキシド 30	70	20	イソプロパノール

		Cleaning solution			Cleaning conditions		Stripper		Stripping conditions		Rinse
		Oxidizing agent Concentration (% by weight)	Organic acid Concentration (% by weight)	Water Concentration (% by weight)	Temperature (°C)	Time (min)	Amine Concentration (% by weight)	Solvent Concentration (% by weight)	Temperature (°C)	Time (min)	
Comparative Example	1	-	-	-	-	-	Monoethanolamine 70	Dimethyl sulfoxide 30	70	20	Isopropanol
	2	-	-	-	-	-	Monoethanolamine 70	Dimethyl sulfoxide 30	90	20	Isopropanol
	3	Hydrogen peroxide 5	-	95	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	20	Isopropanol
	4	-	Oxalic acid 5	95	50	10	Monoethanolamine 70	Dimethyl sulfoxide 30	70	20	Isopropanol

[0018]

[Table 4]

表－４

		剥離性		アルミニウム４腐食性
		レジスト膜６	側壁保護膜５	
比較例	1	×	△	◎
	2	△	◎	△
	3	△	△	◎
	4	×	△	△

		Stripping property		Corrosiveness
		Resist film 6	Sidewall protection film 5	Aluminum wiring element 4
Comparative Example	1	C	B	A
	2	B	A	B
	3	B	B	A
	4	C	B	B

[0019]

[Effect of the Invention]

According to the present invention, a remaining resist and a sidewall protection wall can be removed in an easy and simple manner after dry etching or ashing which follows the dry etching, thereby efficiently manufacturing a semiconductor device.

[Brief Description of the Drawings]

FIG. 1 is a cross-sectional view of a semiconductor device used in examples and comparative examples in which an aluminum wiring element is formed on a semiconductor device substrate by dry etching using a resist film as a mask.

[Description of the Reference Numerals]

1	Semiconductor device substrate
2	Oxidized film
3	Barrier metal (titanium nitride)
4	Aluminum wiring element
5	Sidewall protection film
6	Resist film

[FIG. 1]